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13. ABSTRACT (Maximum 200 words) New methods of controlling the orientation of both low molecular weight and polymeric amphiphiles in Langmuir-Blodgett type films have been utilized. New deposition methods have been developed which differ from both the conventional Langmuir-Blodgett technique and the Langmuir-Schaefer technique. Combination of vertical deposition techniques with the new horizontal penetration method can yield high polarity perpendicular to the film surface. Also, controlled vertical deposition of polymers leads to chain alignment in the deposition direction. This orientation is maintained through further treatment, even if the resulting film is amorphous.			
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MICROPROCESSING-CONTROLLED ORIENTATION IN ULTRATHIN FILMS

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Abstract

New methods of controlling the orientation of both low molecular weight and polymeric amphiphiles in Langmuir-Blodgett type films have been utilized. New deposition methods have been developed which differ from both the conventional Langmuir-Blodgett technique and the Langmuir-Schaefer technique. Combination of vertical deposition techniques with the new horizontal penetration method can yield high polarity perpendicular to the film surface. Also, controlled vertical deposition of polymers leads to chain alignment in the deposition direction. This orientation is maintained through further treatment, even if the resulting film is amorphous.

Introduction

Methods of obtaining ultrathin films with dipoles oriented in one direction perpendicular to the film have been the subject of research effort over the past twenty years. Such orientation in a noncentrosymmetric structure is essential for a material to exhibit a pyroelectric (heat sensor) or piezoelectric (pressure sensor) response or exhibit second order nonlinear optical properties [second harmonic generation (SHG)]. When the Langmuir-Blodgett (1) deposition technique (see figure 1a) is utilized Y deposition usually occurs. Unfortunately Z & X (see figure 1a) deposition usually lead to Y structure because of molecular layer turnaround (2,3), which has been shown to occur on the uptrip (3). To prevent the turnaround a number of approaches have been attempted, including chemical substitution in the hydrophobic tail, (4) polymerizing the amphiphiles at various stages of the process, (3) and alternating multilayers such as acids and amines (5,6). In this paper we will discuss two successful methods, which it is possible to combine, the use of horizontal penetration of the substrate through the gas-water interface, the Day-Lando technique (7) as well as vertical deposition, the Langmuir-Blodgett technique (1), and the use of prepolymerized amphiphiles.

A second type of orientation is required for utilization of ultrathin films in additional types of applications, such as alignment layers in liquid crystal displays. Here orientation in the plane of the film is required. This can be accomplished utilizing the dipping direction in vertical deposition, with parameters such as dipping speed, surface pressure and temperature available for optimization. Since the polymers to be oriented may

well be intractable (polyimides) a soluble low Tg precursor (poly(amic acid)) may be required (8).

Description of Methods

Monolayer manipulations were performed on a commercial Lauda film balance that employs the floating

barrier method of measuring surface pressure. The brass trough was coated with Teflon. An IBM PC was interfaced with the film balance for data acquisition and processing. All the isotherm collection and deposition experiments were done in class 10 laminar flow areas inside a class 100 clean room. Subphase water was obtained from a Millipore water system. In addition, a "shake test" of subphase water in a clean volumetric flask was used to show the complete absence of any tendency to foam; the surface tension is always within the experimental uncertainty of the literature value for pure water. Capillary ripple damping of the pure water in also checked.

The spreading solutions had concentrations of 0.5 to 1 mg/mL in HPLC grade CHCl₃. Initial spreading areas were greater than 70 Å²/molecule and dwell times of 10 min were used to ensure complete evaporation of the spreading solvent. Compression rates were 3.25 cm/min. The water temperature was controlled by circulating thermostated water underneath the brass trough. The temperature of the water in the trough was measured by a surface probe to a precision of ±0.1°C.

Vertical Deposition

The vertical deposition of monolayers onto substrates was achieved via a computer-controlled stepping motor. The motor has 3.9-μm steps and the dipping speed was controlled by the pulse rates of the D/A outputs on the IBM PC. Speeds varying from 0.01 to 50 mm/min can be achieved.

Horizontal Deposition (7)

A hydrophobic substrate was allowed to penetrate through a monolayer in a horizontal orientation. Then the plate was withdrawn vertically to facilitate the draining of the water. In addition, a small tilt angle between the monolayer and substrate was maintained during penetration to prevent air bubbles from being trapped along the surface. For the construction of one component multilayers, the remaining spread monolayer was cleaned off before the

substrate was withdrawn. For the construction of alternating-layer films, the remaining monolayer was cleaned up, and a different monolayer was spread, compressed, and deposited vertically as the substrate was withdrawn.

Substrates

Multilayers were usually deposited on Corning microscope slides. The slides were degreased as follows: pretreated in 70% nitric acid for 12 h and 5 min of ultrasonic agitation in (1) trichloroethylene, (2) acetone, and (3) methanol, respectively. To obtain hydrophobic substrates, the degreased slides were then exposed to hexamethyldisilazane (HMDS) vapor in a glass desiccator for at least 48 h.

Characterization

X-ray diffraction, pyroelectric measurements, nonlinear optical (second harmonic generation and wave guide characteristics), ellipsometric spectroscopy, Fourier transform infrared spectroscopy, dielectric measurements, and atomic force microscopy and optical phase retardation were performed on the ultrathin samples. The materials used will be described in the next section.

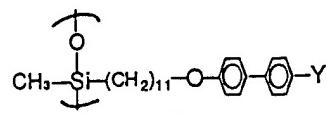
Results and Discussion

Polar Films, it was found that one to one mixtures of the compounds indicated in figure 2(a) formed excellent monolayers at the gas water interface and could be deposited by Z deposition, although pure monolayers containing NO₂ groups aggregated instead of spreading as monolayers. Unfortunately X-ray diffraction of multilayers of single mixed layers resulted in Y type structures, the basic repeat indicating a bilayer structure.

A new method of capitalizing on the hydrophobic nature of the polar NO₂ groups is to employ alternating layers as indicated in figure 2 where the NO₂ group is part of the hydrophylic end in one layer and part of the hydrophobic end in the next layer and so on. As can be seen this should result in multilayer structures in which the NO₂ dipoles are oriented in the same direction. This is confirmed by X-ray diffraction (9) and pyroelectric measurements. Note that the pyroelectric coefficient was determined to be $1.7 \times 10^{-10} \text{ C cm}^{-2} \text{ K}^{-1}$ between 10 and 20°C for ten alternating layers (five bilayers). This is high compared to literature values for multilayers reported in the literature and is less than an order of magnitude less than optimized 10 micrometer poly(vinylidene fluoride) film.

These films could not be used for second harmonic generation (SHG) measurements because the lateral crystallite size approximated the wave length of light. Therefore it was decided to prepare flexible backbone

polymers with nitrobiphenyl groups in the side chain. The one to one copolymer, extensively investigated, is



where Y is O-CH₂-O(CH₂)₂-O-CH₃ and NO₂ in a one to one ratio.

X type horizontal deposition was accomplished as follows. A hydrophobic substrate was penetrated though a monolayer horizontally. The residual monolayer was cleaned up, and then the substrate was withdrawn vertically to facilitate the draining of the water. It should be pointed out that the substrate penetrated through the monolayer horizontally with a small tilt angle to prevent air bubbles from being trapped inside.

The resulting polymer was clearly polar (X layer structure) as determined by X-ray diffraction first order reflection being 3.50nm while the fully extended side chain was calculated to be 3.51 nm. The square root of the second harmonic intensities was linear with multilayer thickness as expected for an SHG material and the $\chi^{(2)}$ value, experimentally determined, agreed with what was expected from the nitrobiphenylether group. Thus polarity is confirmed. The material also is an excellent wave guide (135 layers), k the absorbtion coefficient being essentially zero in the visible range.

The pyroelectric coefficient for this material was very high although there was an unusual variation of the pyroelectric coefficient in the range 19°C to 33°C as well as an unusual peak in ϵ' dielectric measurements in the same temperature range.

Oriented Polymer Multilayers

Polyamide ultra-thin films were prepared using the Langmuir-Blodgett (L-B) technique and their capability of aligning nematic liquid crystals (LC) was evaluated. Characterization of Langmuir and L-B films and of the alignment properties of these films was performed. The precursor method was used for the preparation of the L-B films and the stability of the monolayer of polyamic alkyl amine salt (PAAS) at the air-water interface was evaluated for two different types of amines, a single-chain tertiary-amine and a multichain tertiary-amine. Isotherm measurements showed that the PAAS monolayers in both cases were very stable with a better stability for the later due to the better packing of the side chains. The polyimide L-B films were prepared by vertical deposition and subsequent chemical treatment of the PAAS monolayers (see figure 3). Y-type films were obtained. The molecular anisotropy of the films prior to and after imidization was investigated using Fourier transform infrared spectroscopy FT-IR and optical phase retardation. It was observed that the polymer chains are oriented along the dipping direction

but the degree of orientation does not depend upon the dipping speed nor the surface pressure in the range studied. The morphology of the polyimide L-B films was investigated using X-ray diffraction. The results showed that these films are essentially amorphous. From X-ray reflectivity experiments the thickness of the polyimide monolayer was determined to be 0.47 nm. Atomic force microscopy of a 5-layer film on mica showed that the molecules are aligned along the dipping direction. These films were utilized successfully as alignment layers in twisted nematic display cells.

Acknowledgments

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References

- (1) K.B. Blodgett, *J. Am. Chem. Soc.*, 57, 1007 (1935).
- (2) I. Langmuir, *Science*, 87, 493 (1938).
- (3) V. Enkelmann and J.B. Lando, *J. Polym. Sci., Polym. Chem. Ed.*, 15, 1843 (1977).
- (4) R. Popovitz-Biro, K. Hill, E. Sharit, D. Hung, M. Lahav, L. Leiserowitz, J. Sagiv, H. Hsiung, G.R. Meredith and H. Vanherzeele, *J. Am. Chem. Soc.*, 112, 2498 (1990).
- (5) M.F. Daniel, G.W. Smith, *Mol. Cryst. Liq. Cryst.* 102, 193 (1984).
- (6) S.P. Walsh and J.B. Lando, *Langmuir*, 10, 246 (1994).
- (7) D.R. Day and J.B. Lando, *Macromolecules*, 13, 1478 (1980).
- (8) M. Kakimoto, M. Suzuki, T. Konishi, Y. Imai, M. Iwamoto, and T. Hino, *Chem. Lett.*, 823 (1986).
- (9) S. H. Ou, V. Percec, J. A. Mann, Jr. and J.B. Lando, *Langmuir* 10, 905 (1994).
- (10) A. Albarici, Master of Science Thesis, "Langmuir Blodgett Films as Alignment Layers for Nematic Liquid Crystal Displays," Case Western Reserve University, December 1994.

Figures

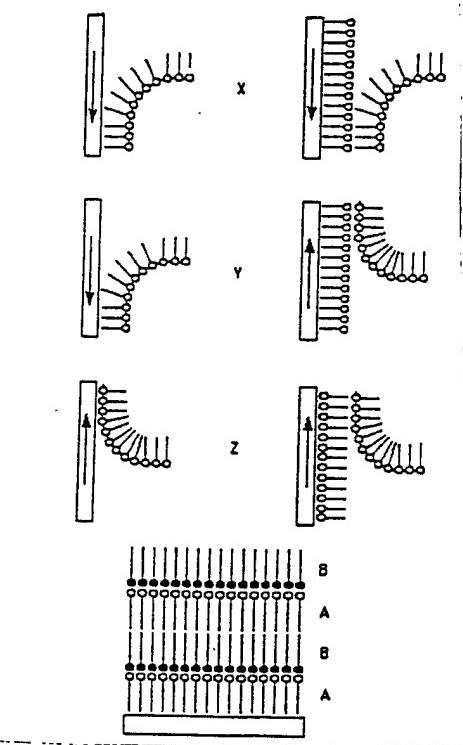


Figure 1. (a) Possible deposition types for a hydrophobic substrate: A, X, Y, and Z deposition; B, repeat pattern for y layers. (b) A Y-type ABAB LB multilayer film.

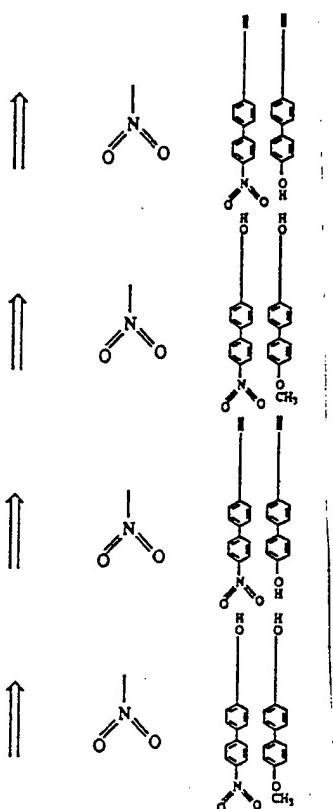


Figure 2. Schematic showing the construction of nitrobiphenyl dipole moments by an untraditional alternating-layer method.

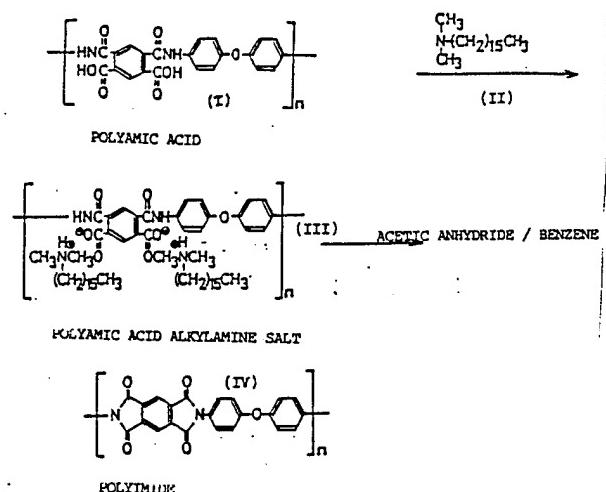


Figure 3. Polymimides by the precursor method.

Key Word/Phrase Index

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